Covalent Crosslinking of Carbon Nanotube Materials for Improved Tensile Strength

September 9, 2013

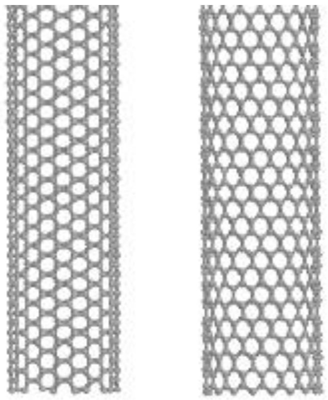
James S. Baker, Sandi Miller, Tiffany Williams, Michael Meador

Postdoctoral Research Fellow

NASA Glenn Research Center, Cleveland, Ohio

Carbon Nanotubes

SWCNT



Source: Dai, H. *Acc. Chem. Res,* **2002**, *35*, 1035

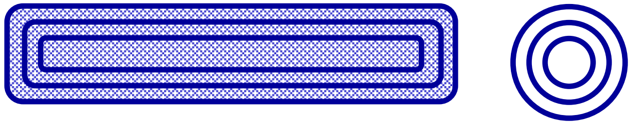
Cylindrical structure of *sp*^{2} hybridized carbon atoms

Diameters- 1-50 nm
Lengths- 100nm- ~1 mm

Single-walled (SWCNT) or Multi-walled (MWCNT)

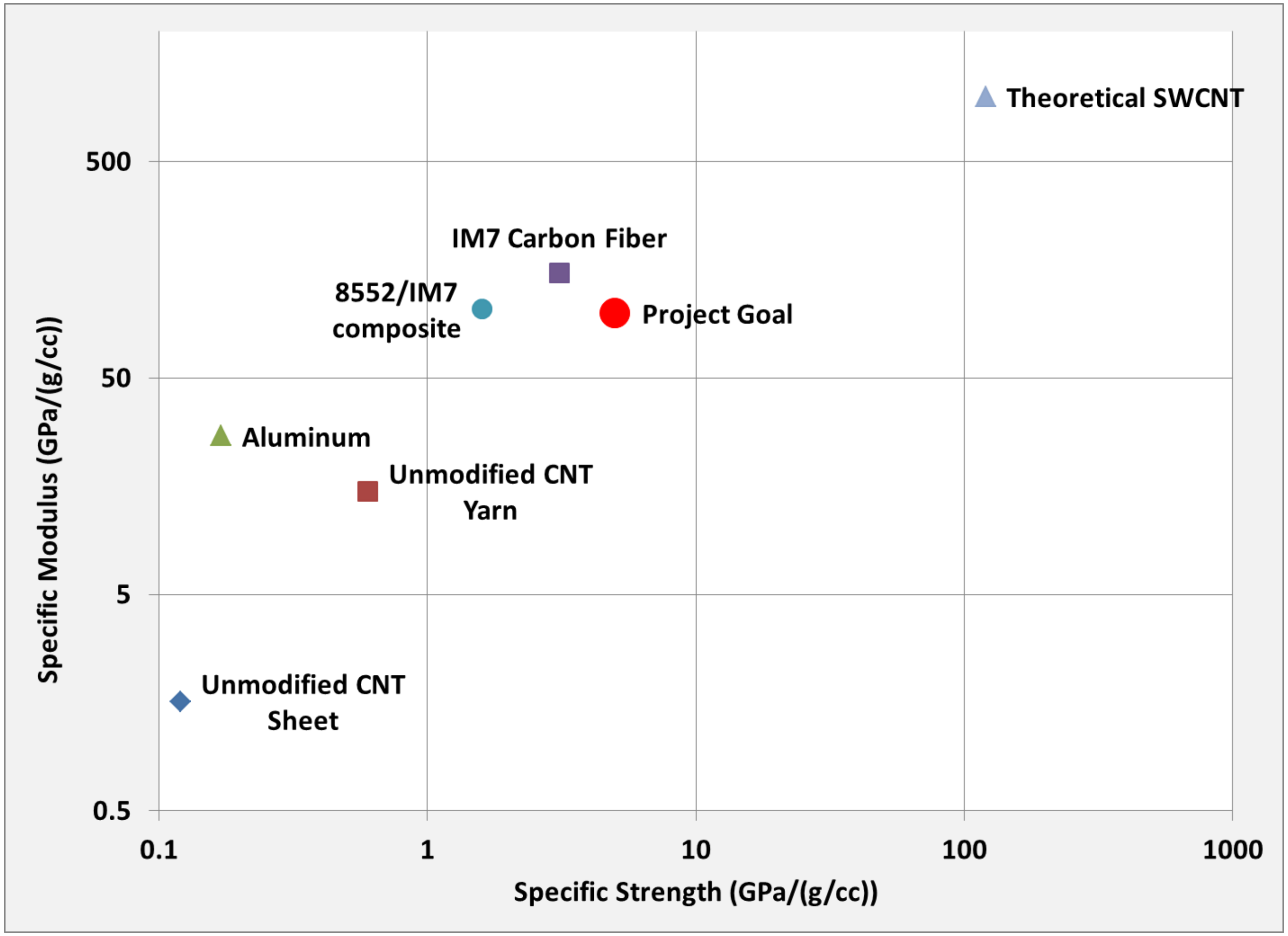
Properties:
- High strength and stiffness
- Low density (~1.6-2.2 g/cm^3)
- Good thermal and electrical conductivity
- High thermal stability

MWCNT



Naraghi, M.; Filleter, T.; Moravsky, A.; Locascio, M.; Loutfy, R.; Espinosa, H. *ACS Nano*, **2010**, *4*, 6463-6476
Lu, W.; Zu, M.; Byun, J-H.; Kim, B-S.; Chou, T-W. *Adv. Mater.*, **2012**, *24*, 1805-1833

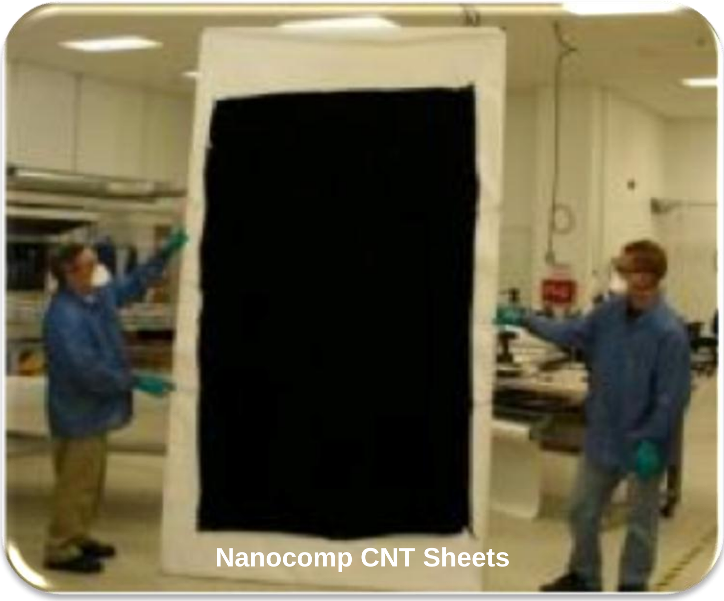
Project Goal



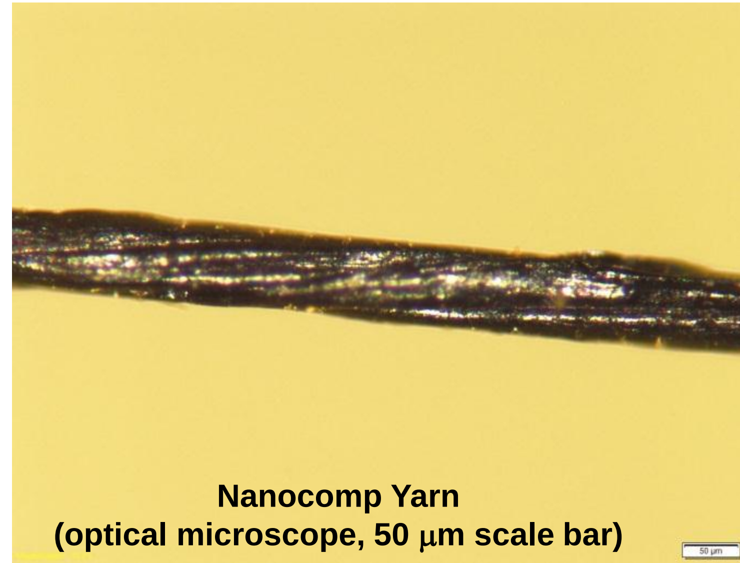
Improve strength to weight ratio of polymer matrix composite materials

- Reduce vehicle dry weight
  - ✓ Increase payload capacity
  - ✓ Lower fuel consumption

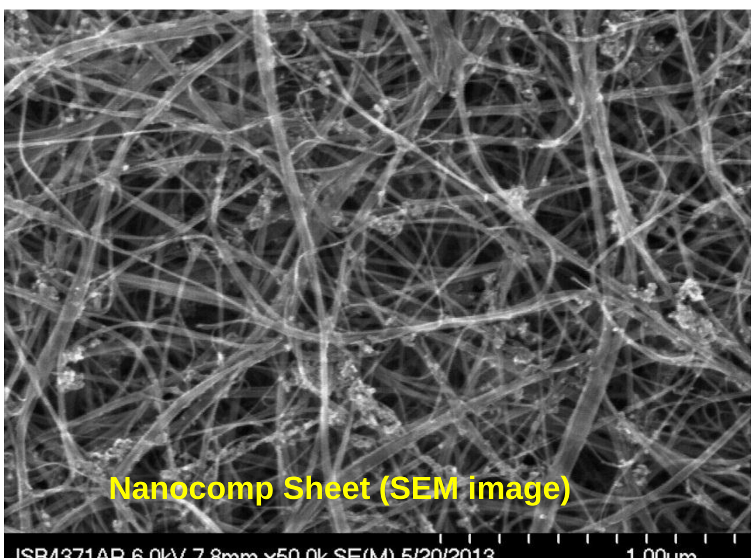
Carbon Nanotube Materials



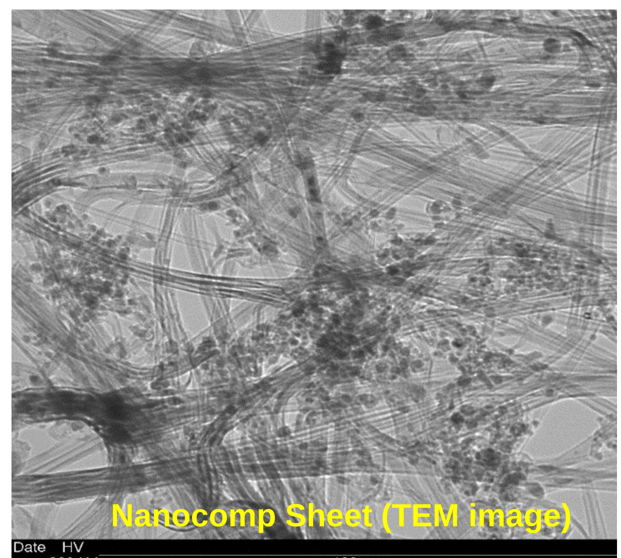
Nanocomp CNT Sheets



Nanocomp Yarn
(optical microscope, 50 μm scale bar)

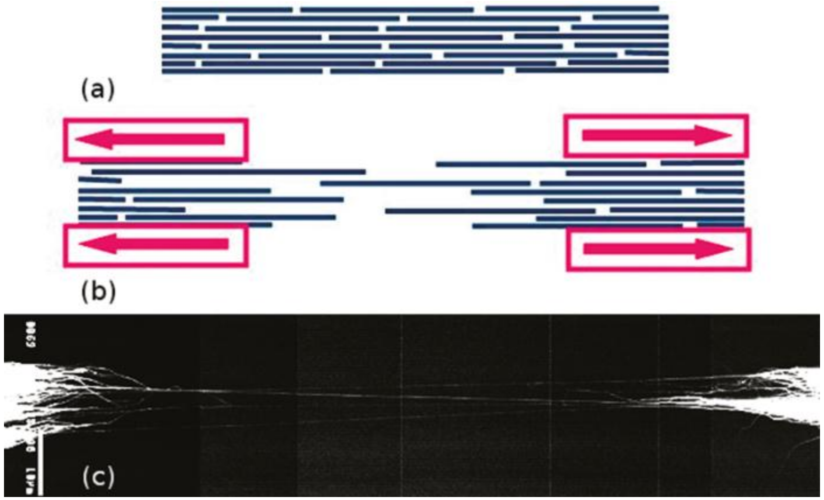


Nanocomp Sheet (SEM image)



Nanocomp Sheet (TEM image)

Carbon Nanotube Yarns



Source: Vilatela,J.; Elliott, J.; Windle, A. *ACS Nano* **2011,** *3*, 1921-27

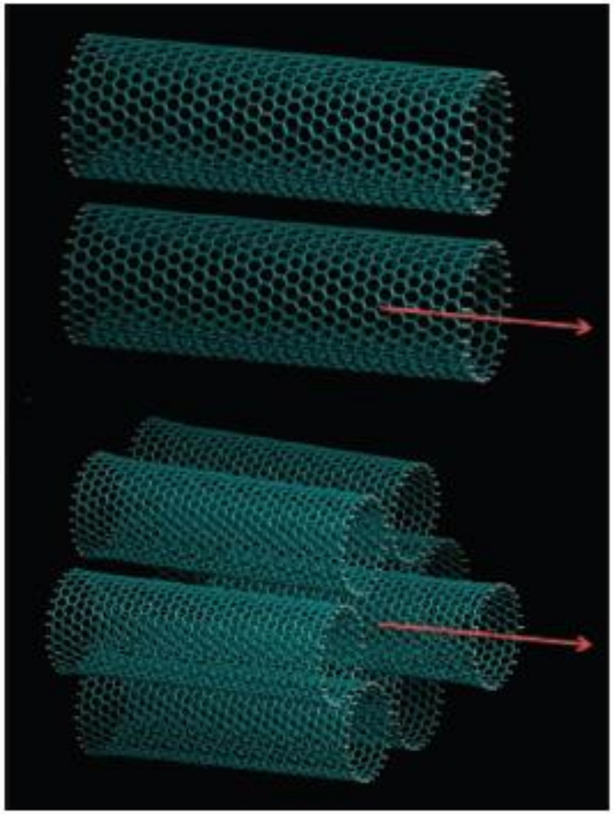
Carbon Nanotube tensile strength ~10-100 GPa

State-of-the-art carbon nanotube yarns ~3 GPa

Failure from slippage of nanotubes/bundles, not breakage of nanotubes

Windle, *et al*. (*Adv. Mater.,* **2010**, 4959; *ACS Nano*, **2011**, 9339)

Carbon Nanotubes



Nanotube tensile strength~ 10-100 GPa

Inter-tube shear force= 0.5-10 MPa

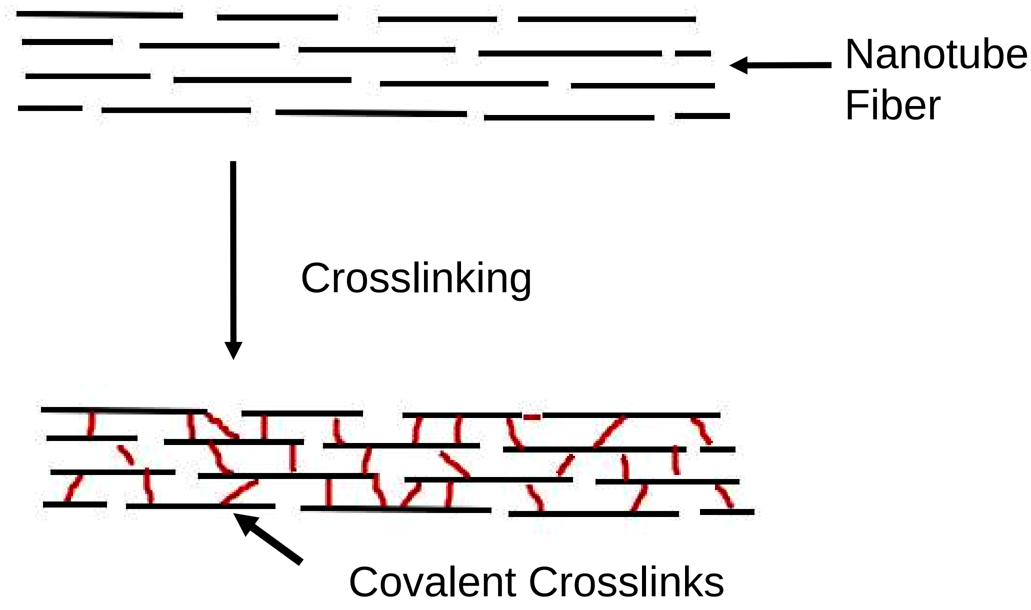
Ease of sliding leads to poor load transfer between nanotubes

Need to increase inter-nanotube forces to take full advantage of nanotube tensile properties

Source: Filleter, T.; *et al*. *Nano Lett.*, **2012**, *12,* 732

Filleter, T.; Espinosa, H.D. *Carbon*, **2013**, *56*, 1-11

Our Proposed Solutions



Create covalent, inter-tube bonds to prevent tube-tube sliding.

- Chemical modification
- Electron beam irradiation

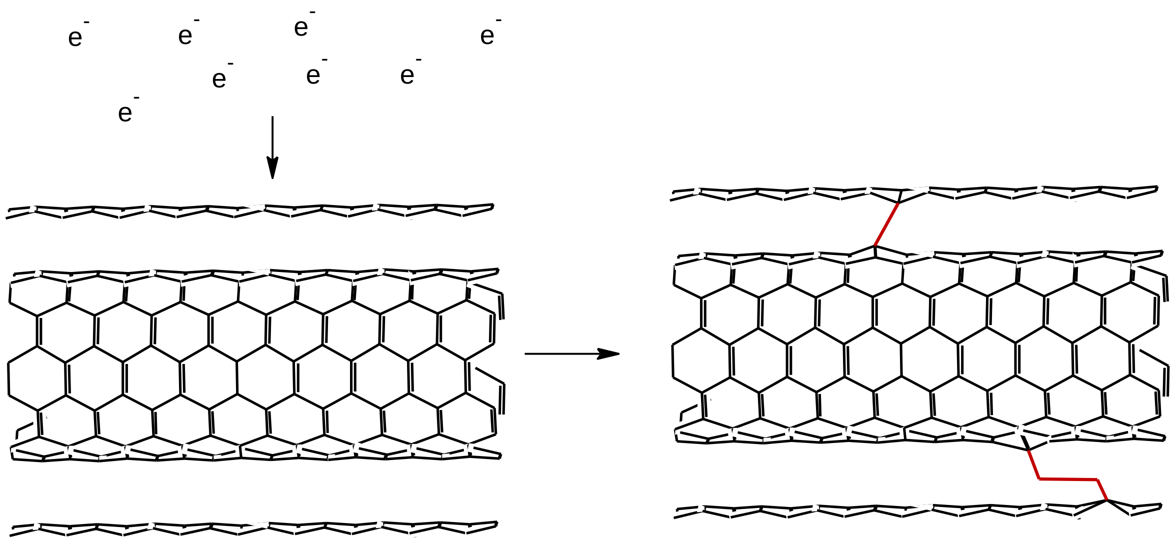
Increase inter-tube contact and alignment

- Solvent densification
- Stretching

Minimize damage to nanotubes during modification

Electron Beam Crosslinking

Irradiation of carbon nanotubes with high-energy particles can produce inter-shell or inter-nanotube covalent bonds

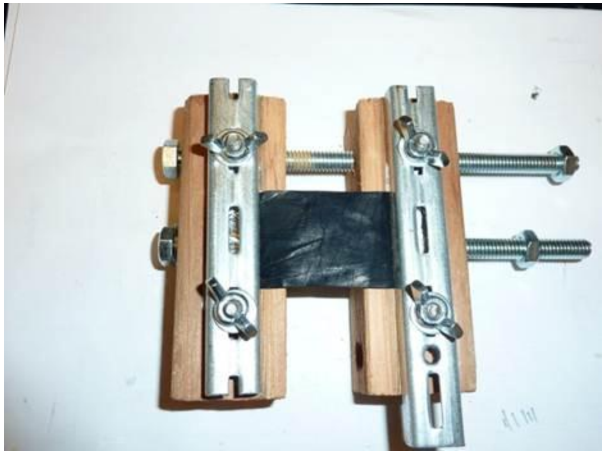


Filleter, T.; Espinosa, H. *Carbon*, **2013**, *56*, 1-11
Espinosa, H.; Filleter, T.; Naraghi, M. *Adv. Mater.*, **2012**, *24*, 2805-2823
Pregler, S.; Sinnott, S. *Phys. Rev. B,* **2006**, *73*, 224106

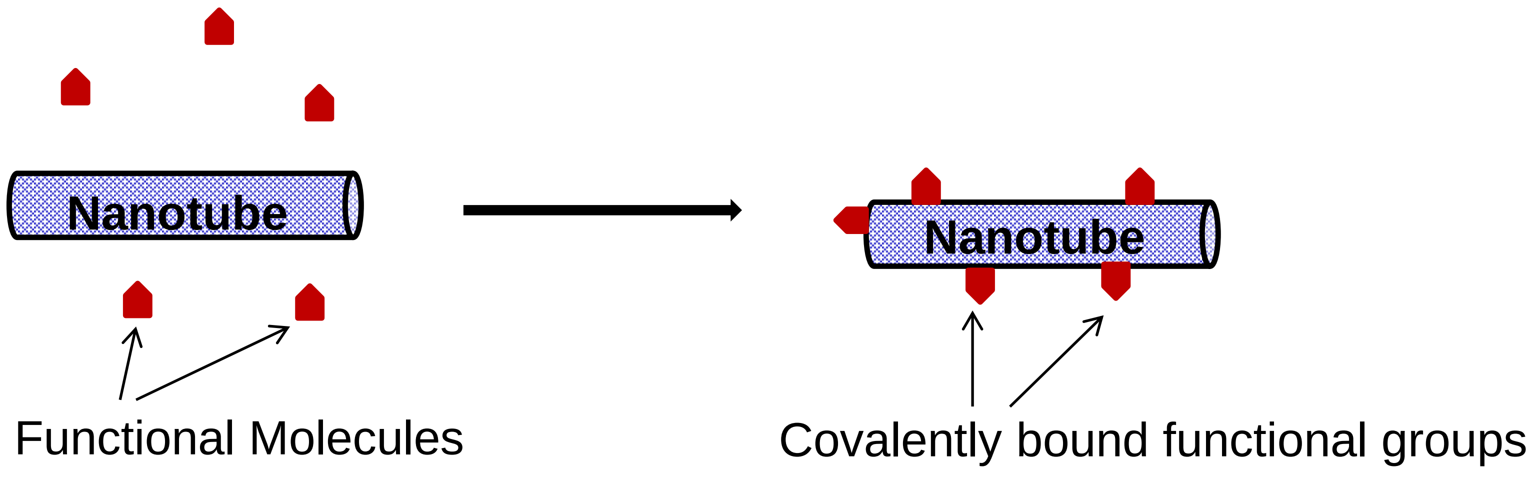
Prestraining

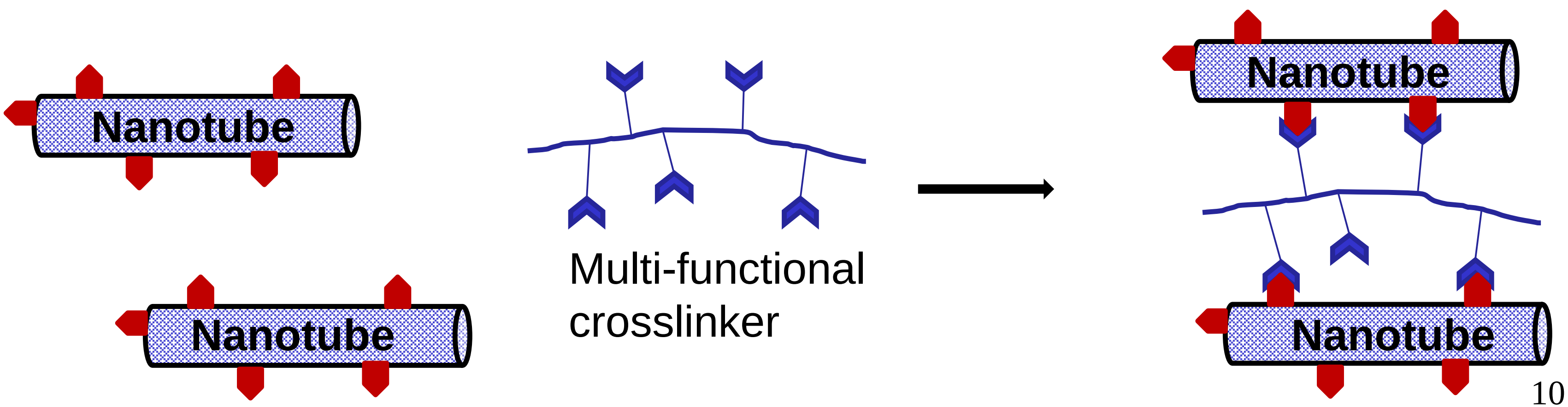
Drawing of yarns during spinning leads to improved nanotube packing and alignment

- Apply same principle to sheet material



Chemical Crosslinking



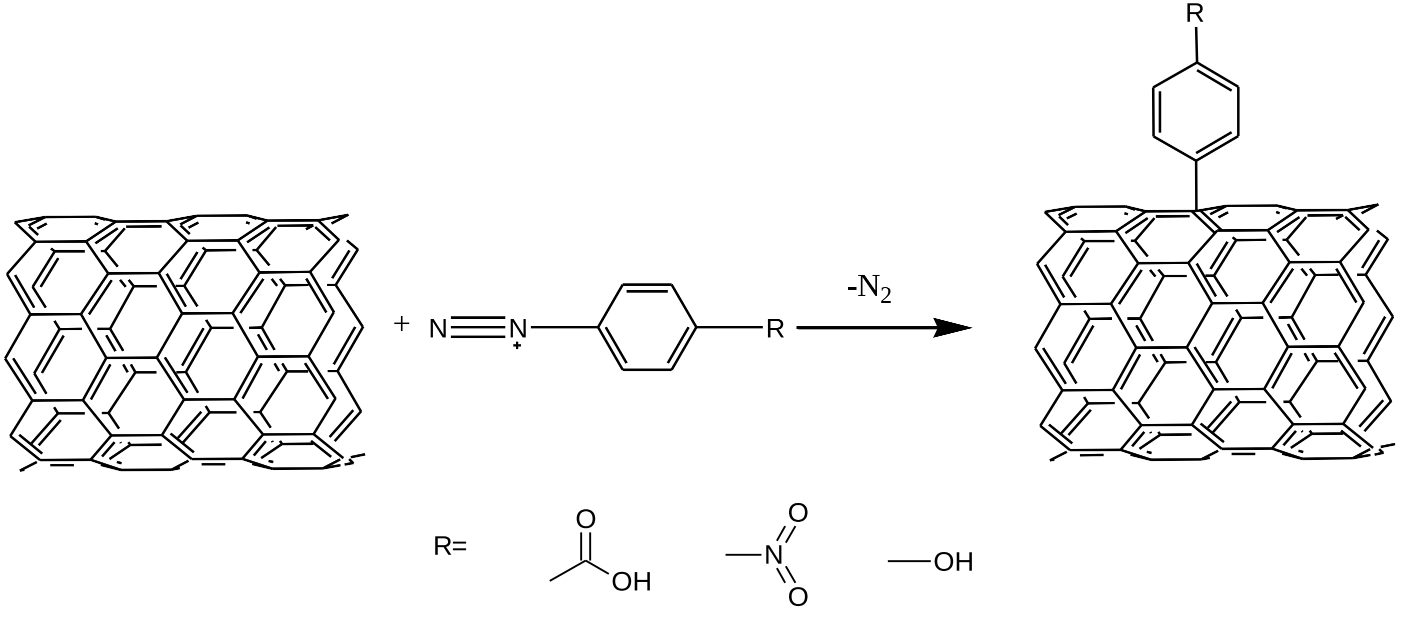


Aryl Diazonium

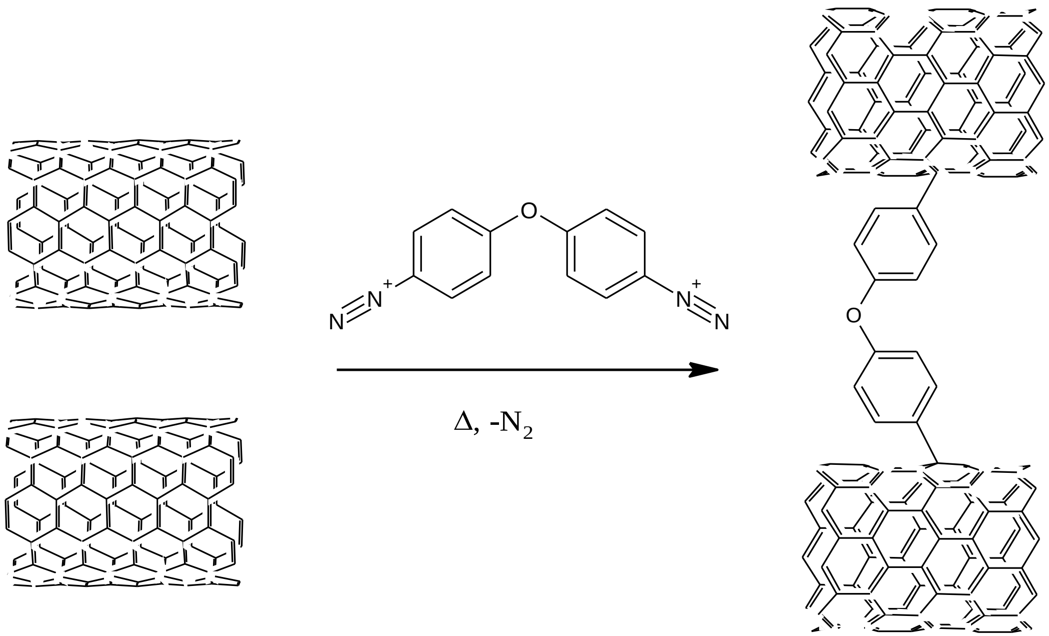
- Commonly used method for covalent functionalization of nanotubes (*Synlett*, **2004**, 155; *JACS*, **2003**, 1156; *Chem. Mater.*, **2001**, 3823)

- Use of *para*-functional anilines allows introduction of functional groups

- Using a di- or multi-amines should allow crosslinking of tubes

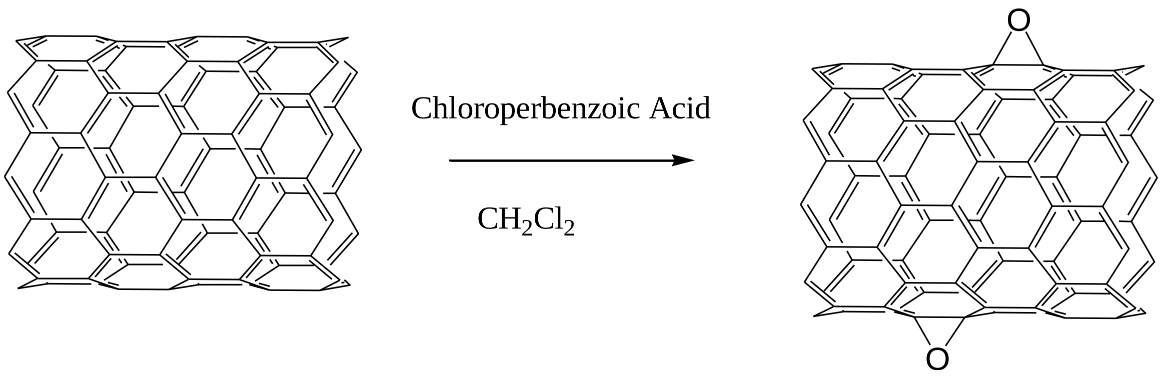


Aryl Diazonium

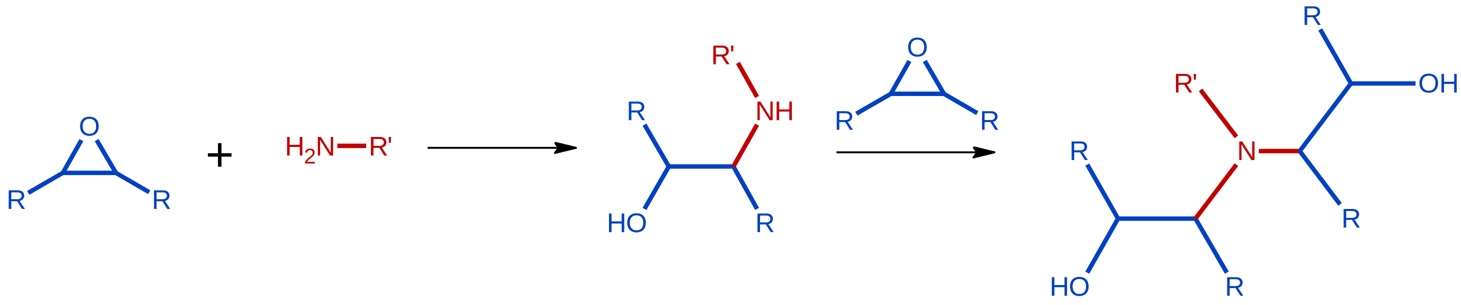


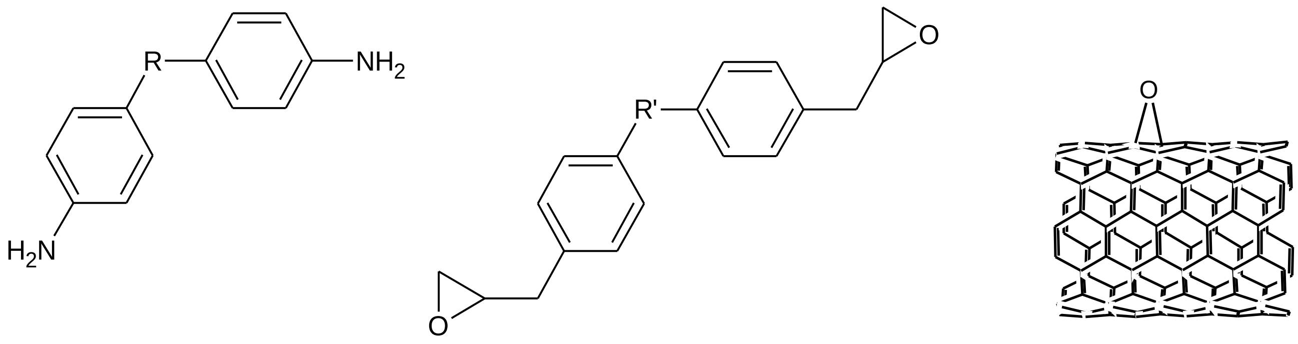
Epoxide Functional Nanotubes

- Reaction with chloroperbenzoic acid (Prilezhaev reaction) can introduce epoxy rings on the nanotube surface (*JACS*, **2006**, 11322; *ACS Appl. Mater. Interfaces*, **2012**, 2065)



Epoxide Functional Nanotubes

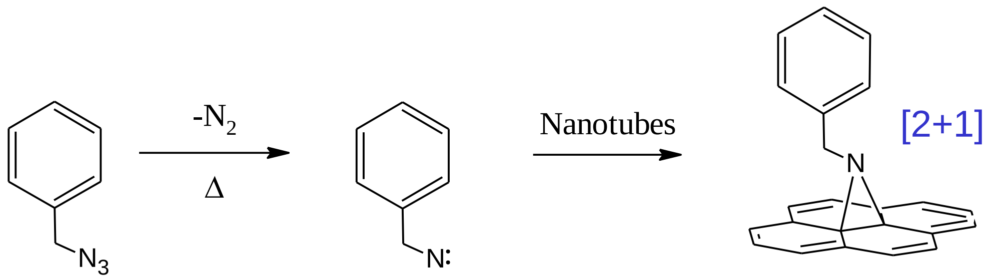




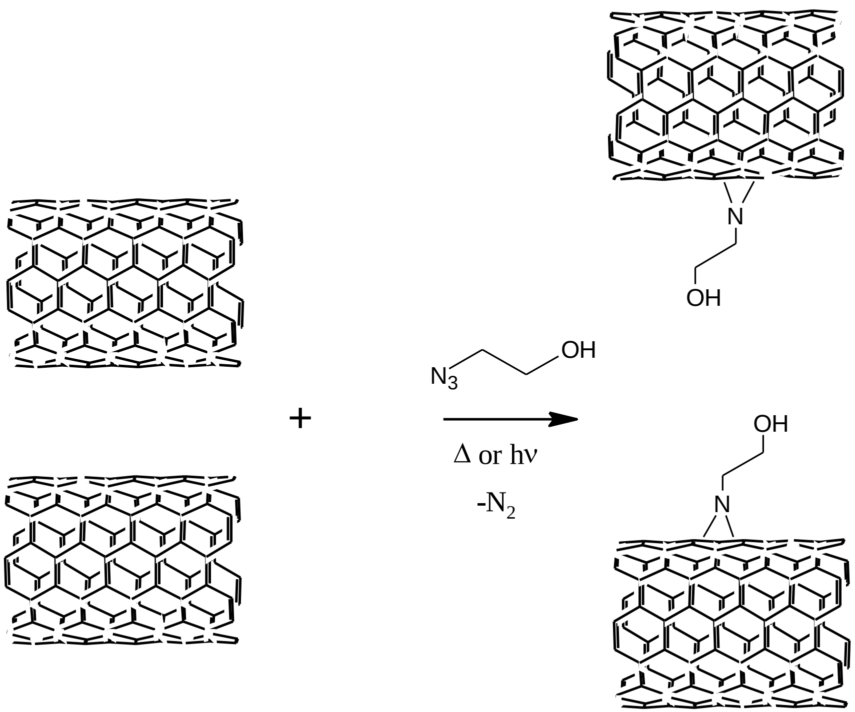
Epoxide rings on nanotubes can react with diamine during resin curing

- covalent attachment of nanotubes to resin matrix

Functionalization Using Nitrenes



[2+1] cycloaddition of nitrene to nanotube walls

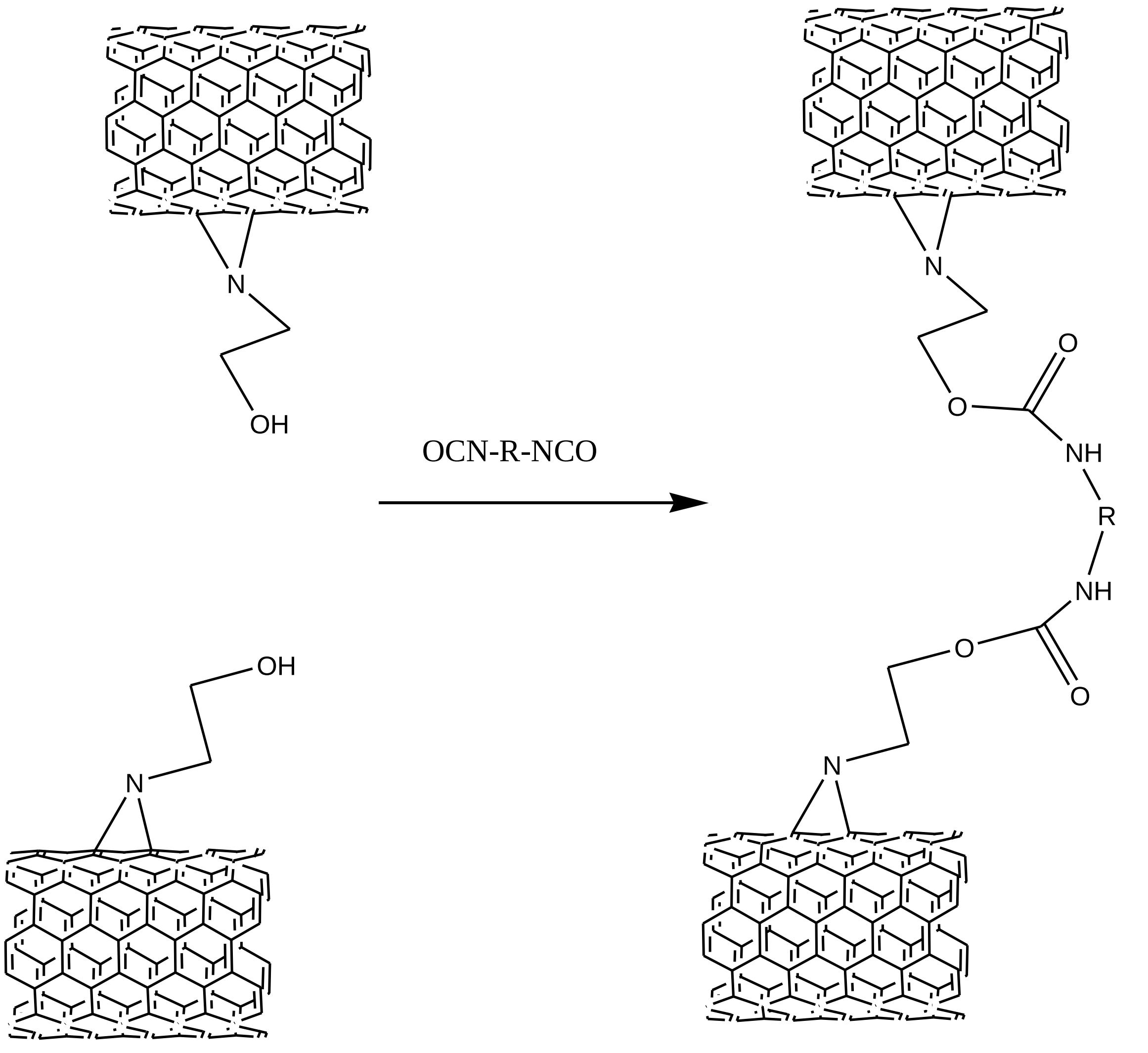


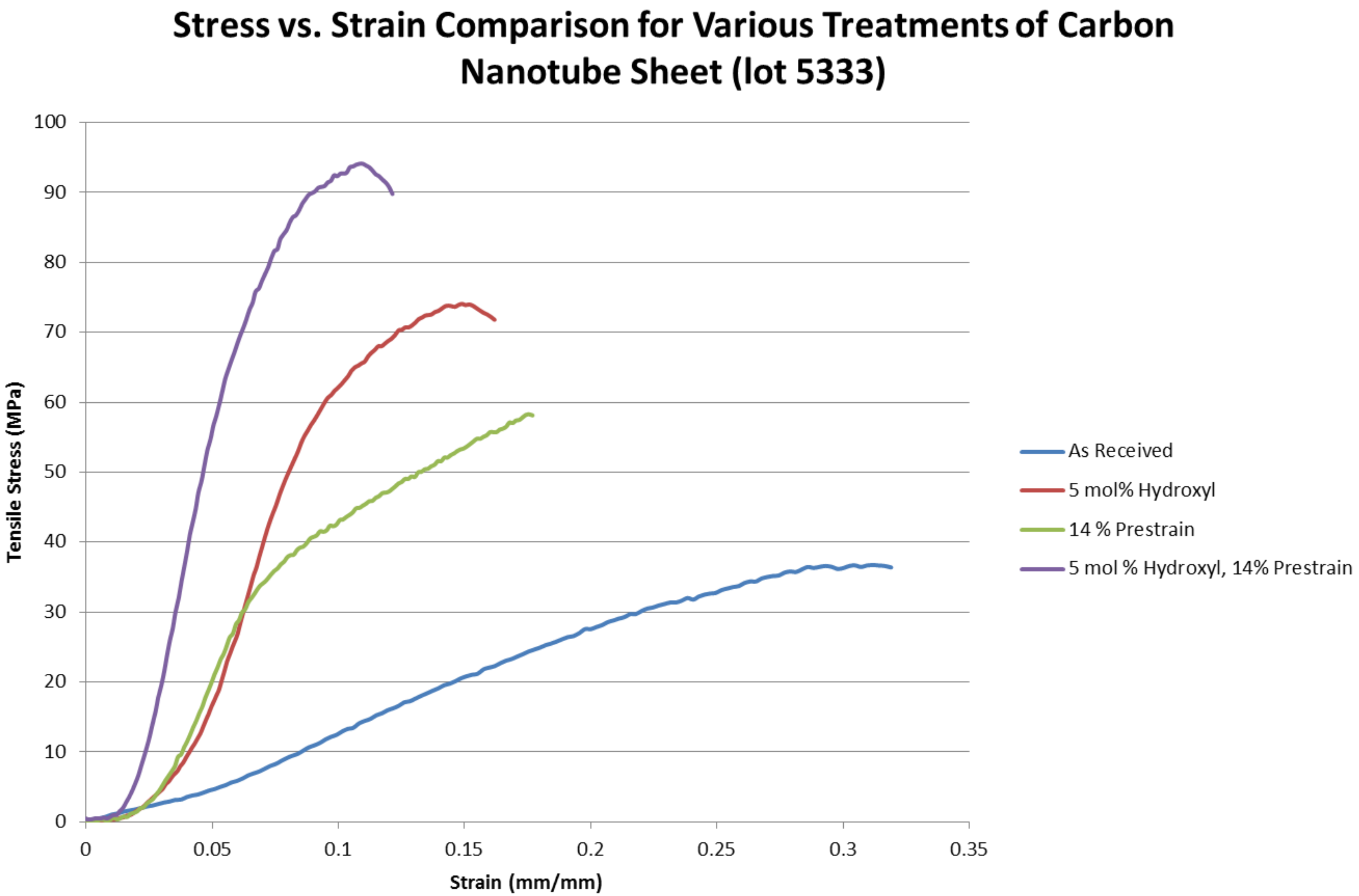
Hydroxyl Functional Nanotubes (CNT-OH)

Similar route for amine (CNT-NH_2)

Holzinger, M.; et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 4002; *JACS*, **2003**, *125,* 8566
Gao, C.; He, H.; Zhou, L.; Zheng, X.; Zhang, Y. *Chem. Mater.*, **2009**, *21*, 360

Nanotube Crosslinking Through Multifunctional Linkers

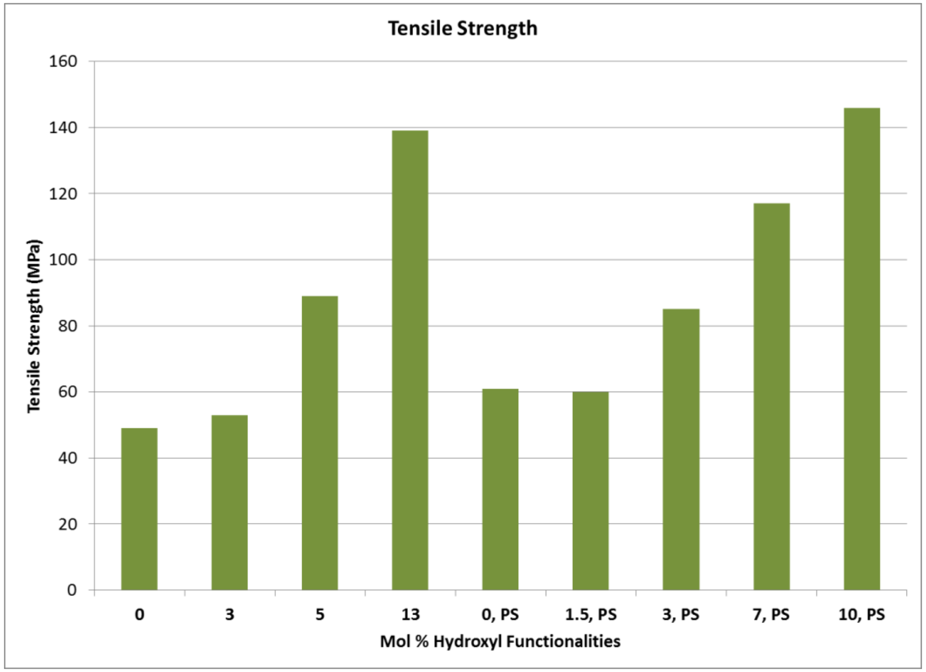


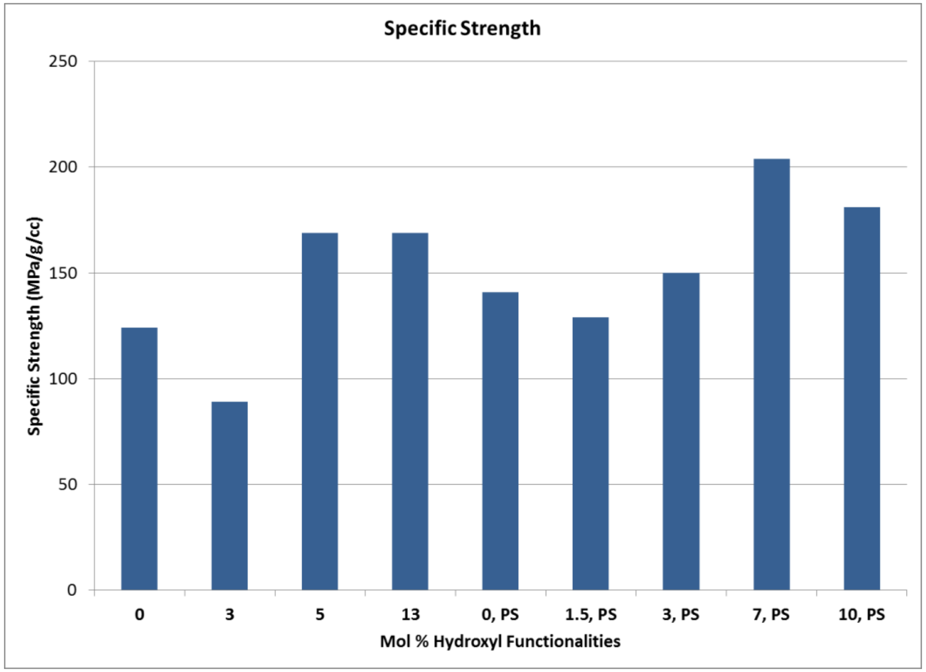


Functionalization results in:

- ✓ Higher tensile strength
- ✓ Higher tensile modulus
- ✓ Lower strain at break

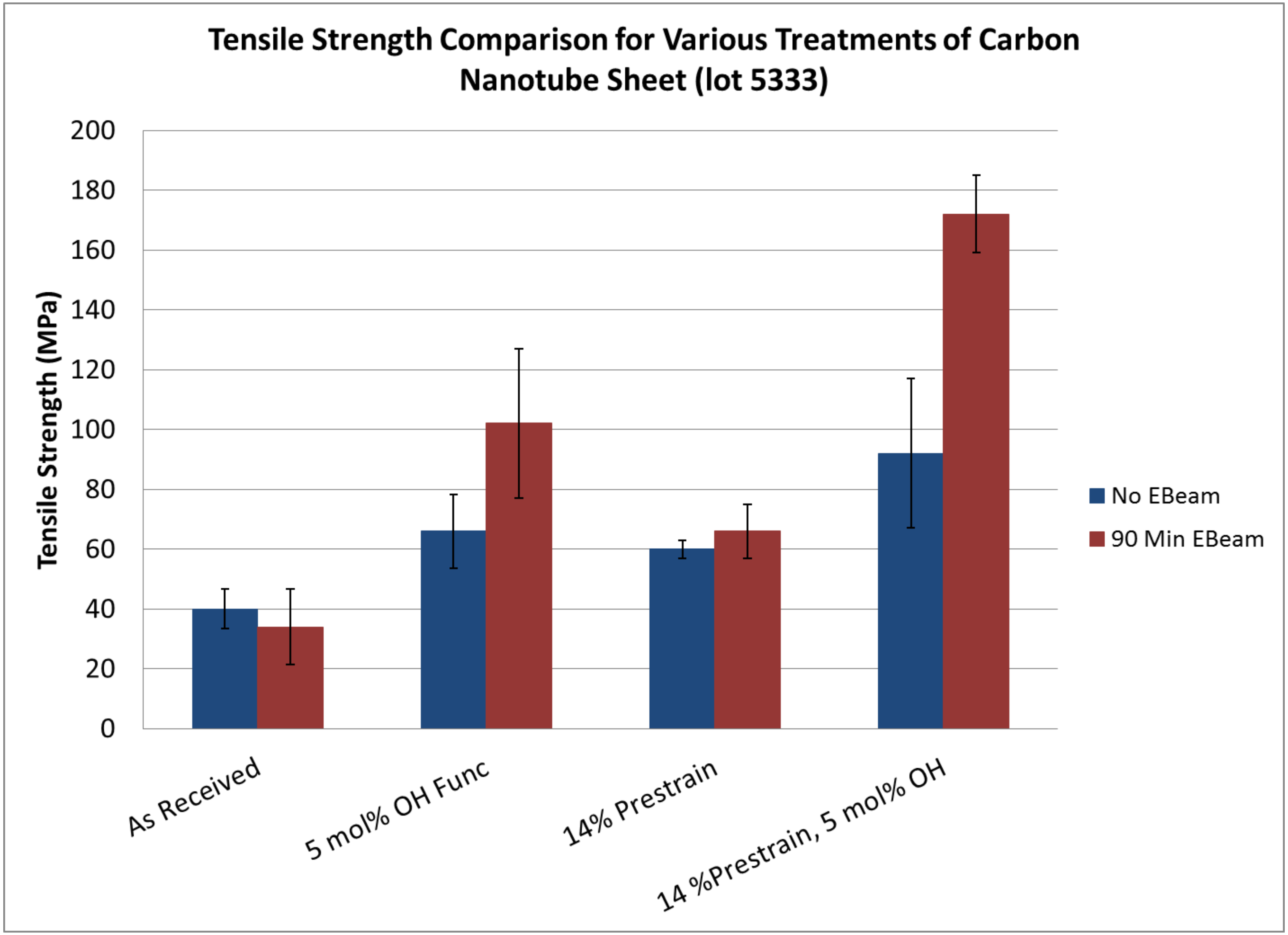
Effect of Degree of Functionalization



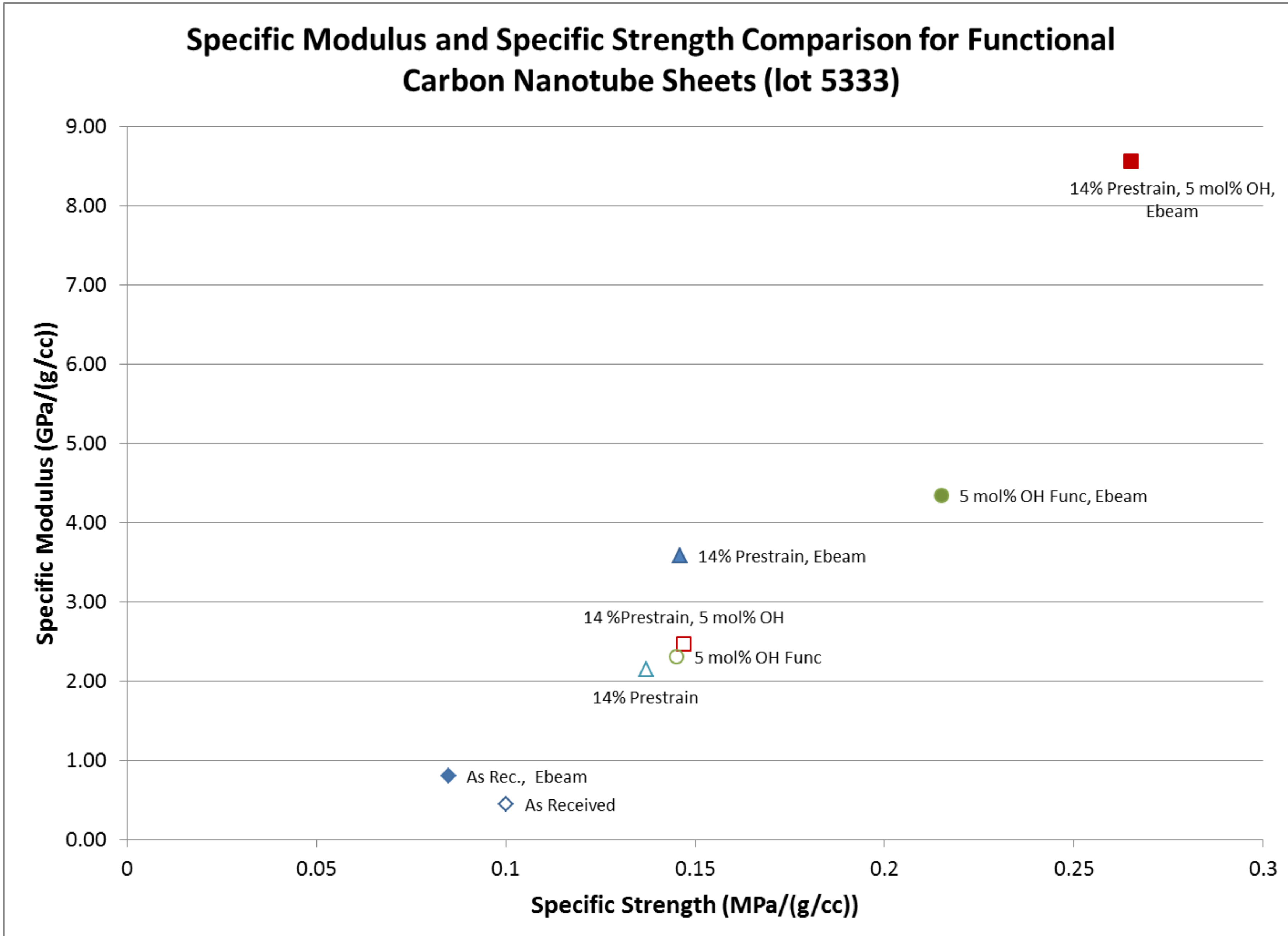


'PS' indicates 14% prestrained

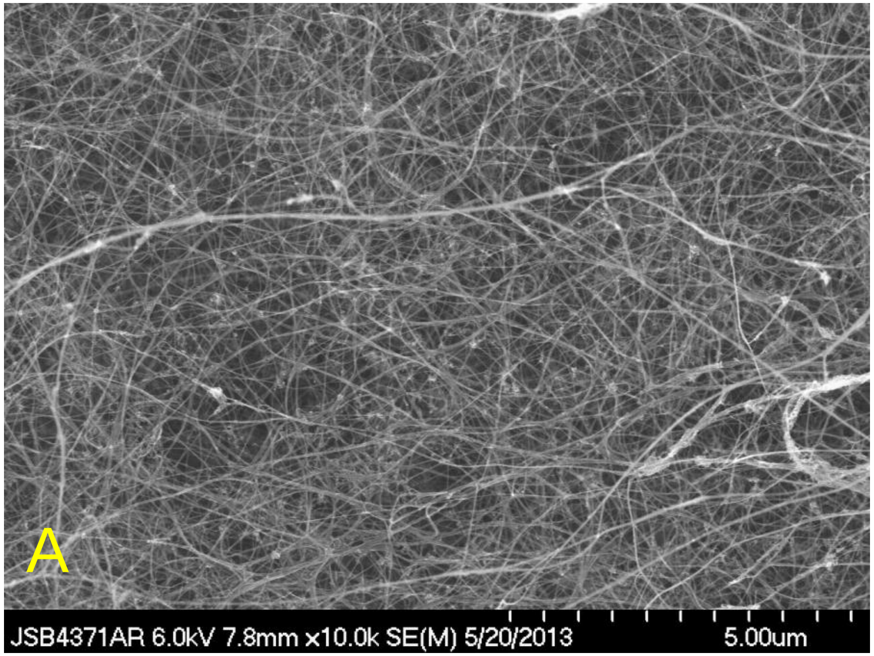
Optimal degree of functionalization is 5-10 mol% for best strength:weight ratio



Hydroxyl functional material prepared by reaction with azido ethanol (nitrene route)
E Beam irradiation, 90 min exposure, 2.2x 10^{17} e^{-} /cm^{2} total fluence


Specific Modulus and Specific Strength Comparison for Functional Carbon Nanotube Sheets (lot 5333)
Specific Modulus (GPa/(g/cc))
Specific Strength (MPa/(g/cc))
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
0.05
0.1
0.15
0.2
0.25
0.3
14% Prestrain, 5 mol% OH, Ebeam
5 mol% OH Func, Ebeam
14% Prestrain, Ebeam
14 %Prestrain, 5 mol% OH
5 mol% OH Func
14% Prestrain
As Rec., Ebeam
As Received

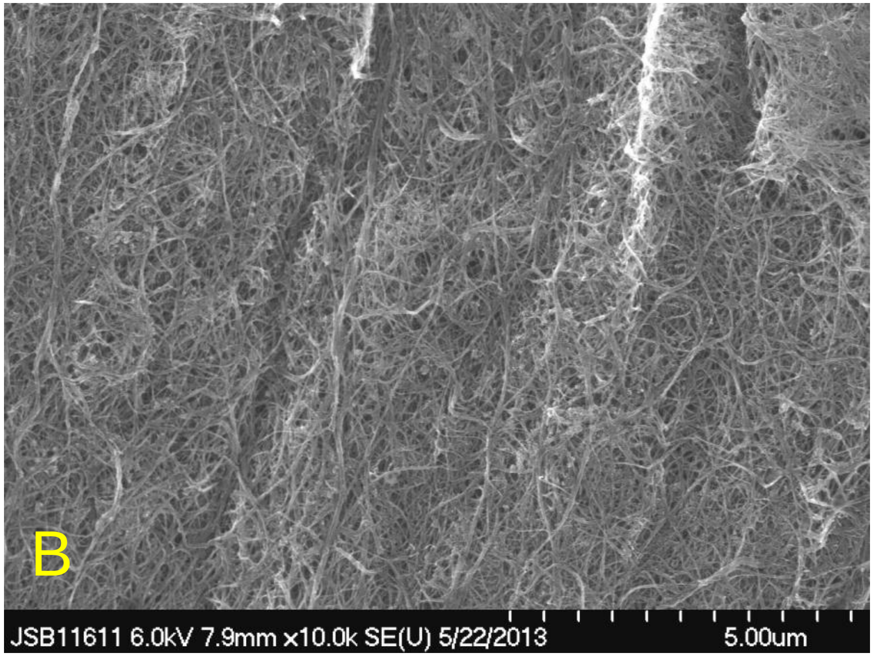
SEM Micrographs of Nanotube Sheet



A. As Received

B. 14% Prestrain, 5 mol% OH

C. 14% Prestrain, 5 mol% OH, 90 min E Beam



SEM Micrographs of Nanotube Sheet

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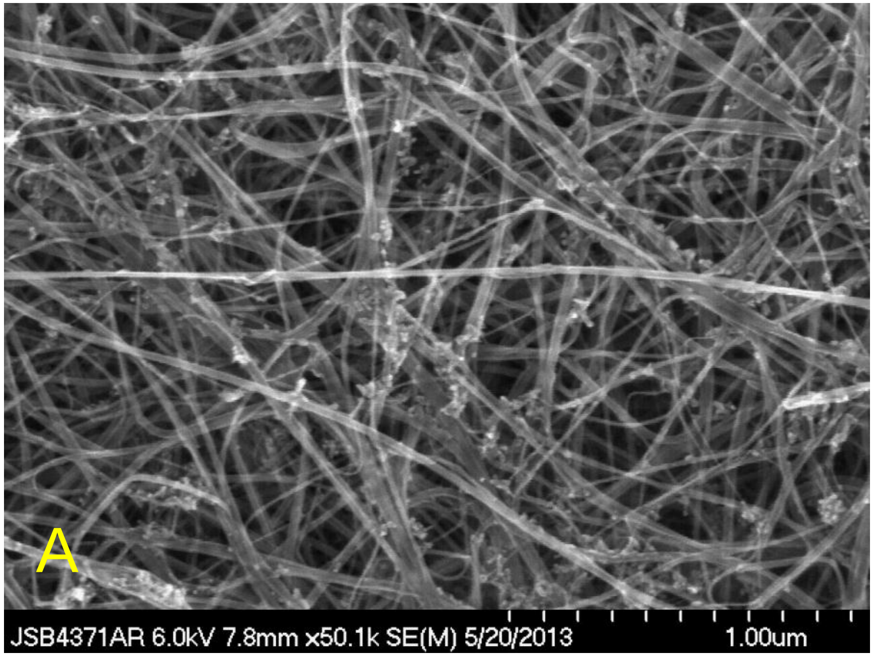
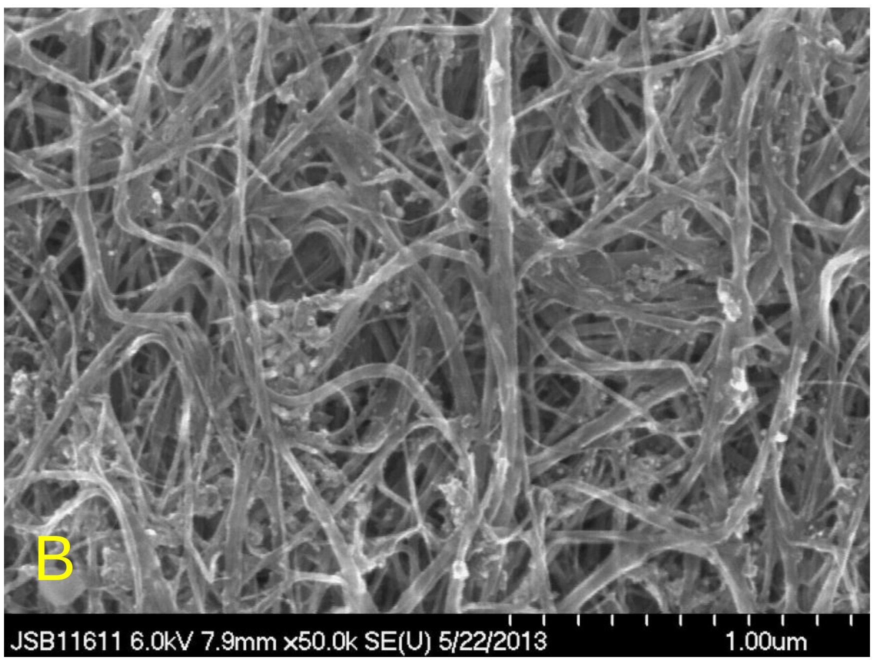
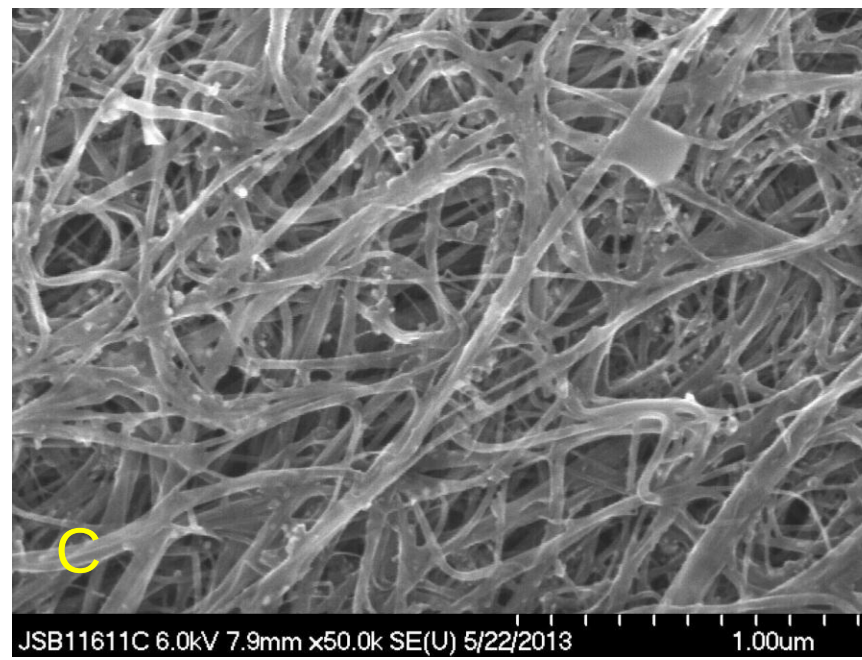






Summary

Several methods were examined that resulted in improved tensile properties for the carbon nanotube sheet material

- ✓ Covalent functionalization and crosslinking
- ✓ Electron beam irradiation
- ✓ Uniaxial prestraining

Generally, the methods evaluated resulted in an increase in material tensile strength and modulus and a decrease in strain at failure

Combination of these methods resulted in the largest improvement

> 14 % prestrain, 5 mol% OH, 90 min E Beam resulted in ~150% increase in specific strength and >10-fold increase in specific modulus over the as-received material

Currently evaluating performance of functional nanotube sheet material in polymer matrix composites

Acknowledgements

- Dr. Michael Meador

- Dr. Sandi Miller
- Dr. Tiffany Williams
- Dr. Francisco Sola-Lopez
- Dr. Marisabel Lebron-Colon
- Dr. Jim Gaier

- Daniel Scheiman, Nate Wilmoth, Linda McCorkle

- Prof. Roberto Uribe (Kent State), NEO Beam electron beam facility

- Fellowship Funding- NASA Postdoctoral Program administrated by Oak Ridge Associated Universities

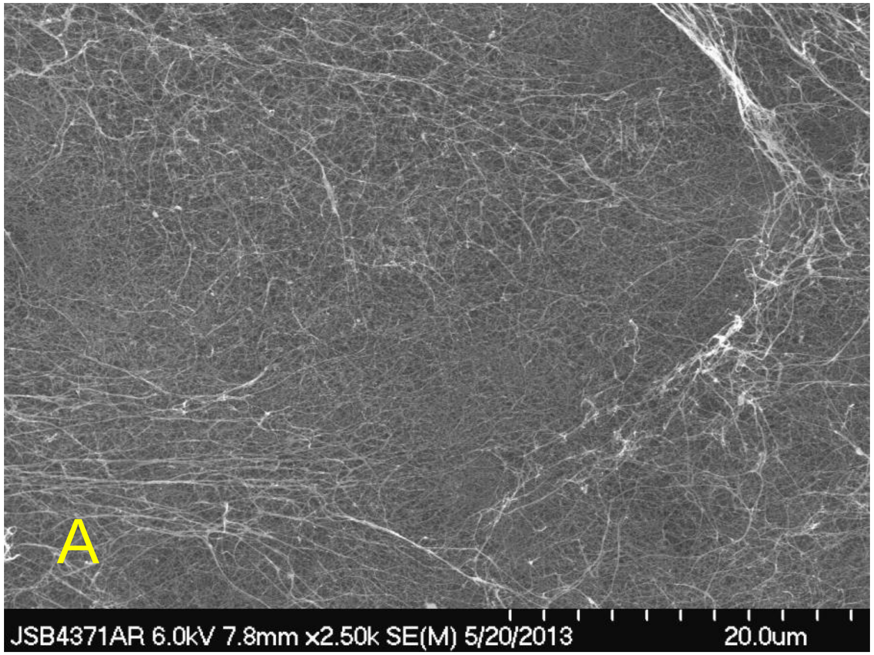
- Project Funding- NASA Space Technology Game Changing Development Program

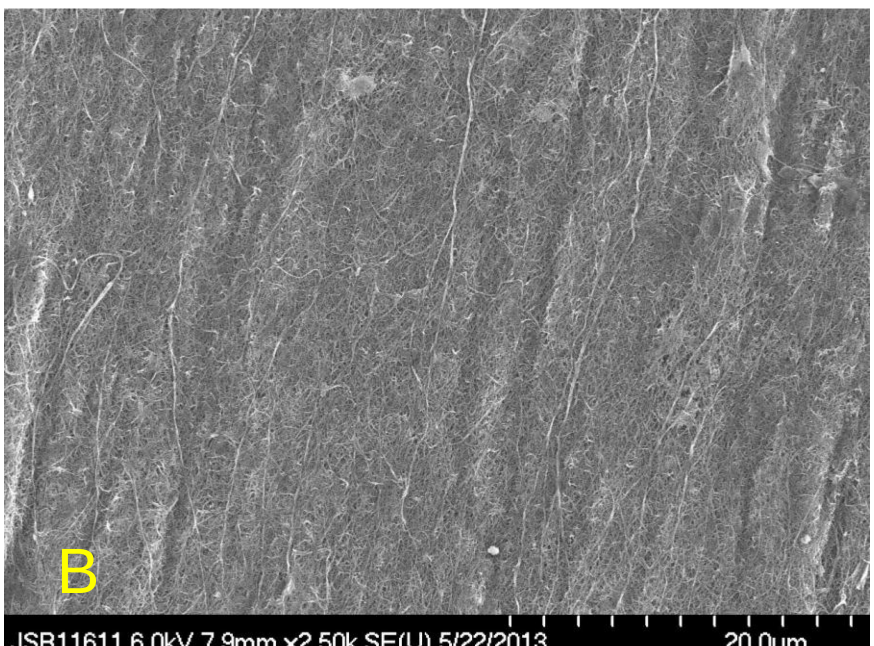
SEM Micrographs of Nanotube Sheet

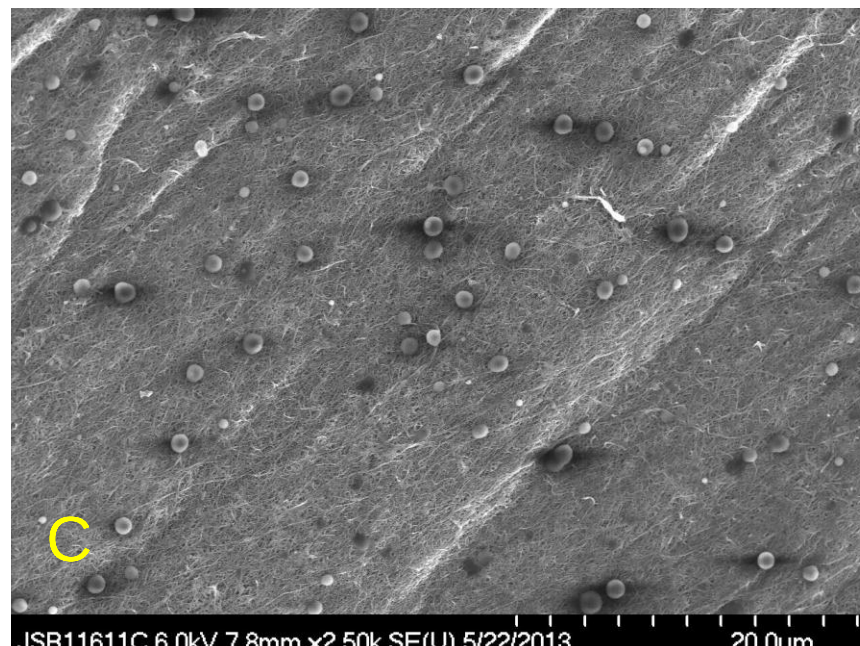
A. As Received

B. 14% Prestrain, 5 mol% OH

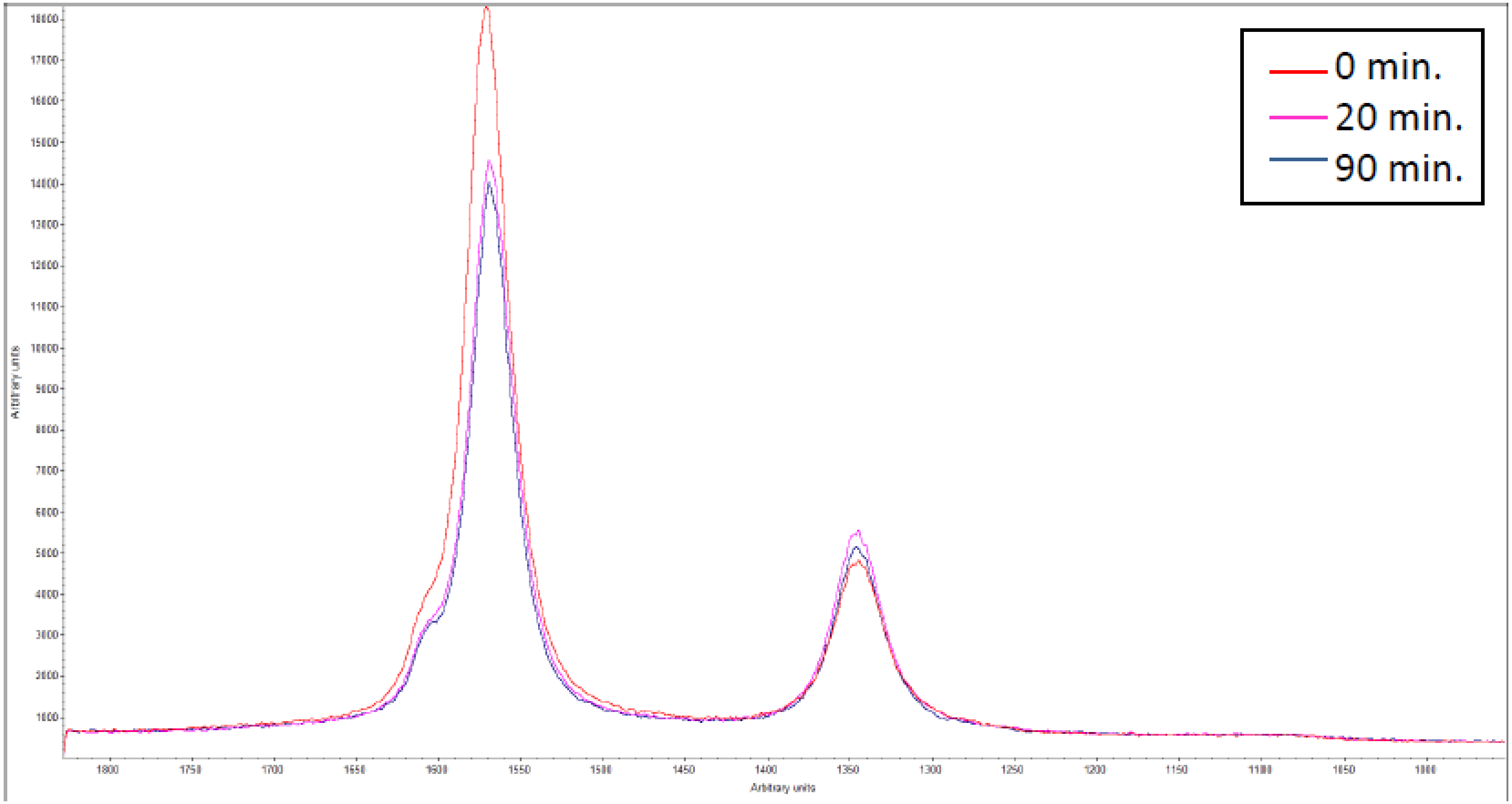
C. 14% Prestrain, 5 mol% OH, 90 min E Beam





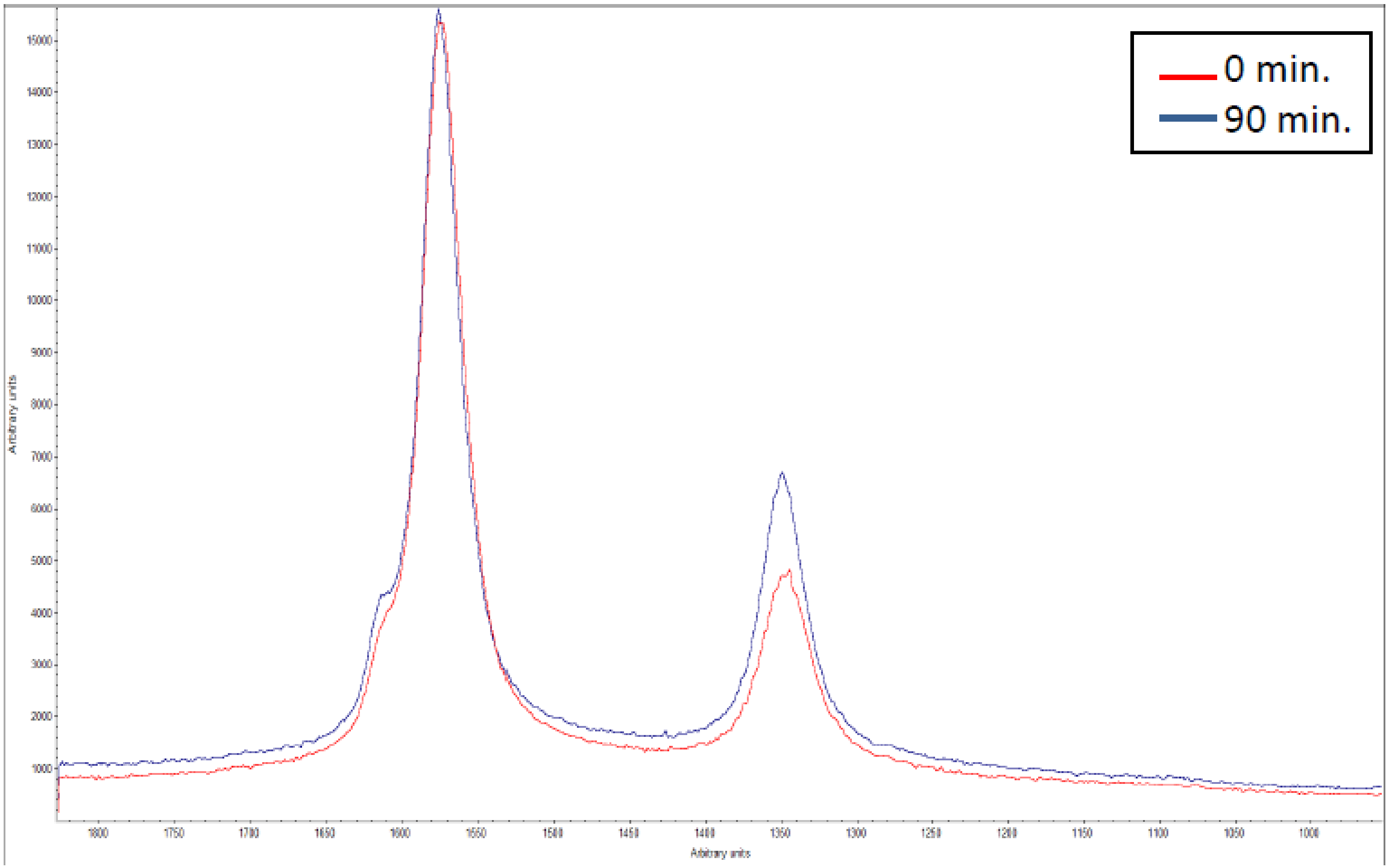


AR #5333



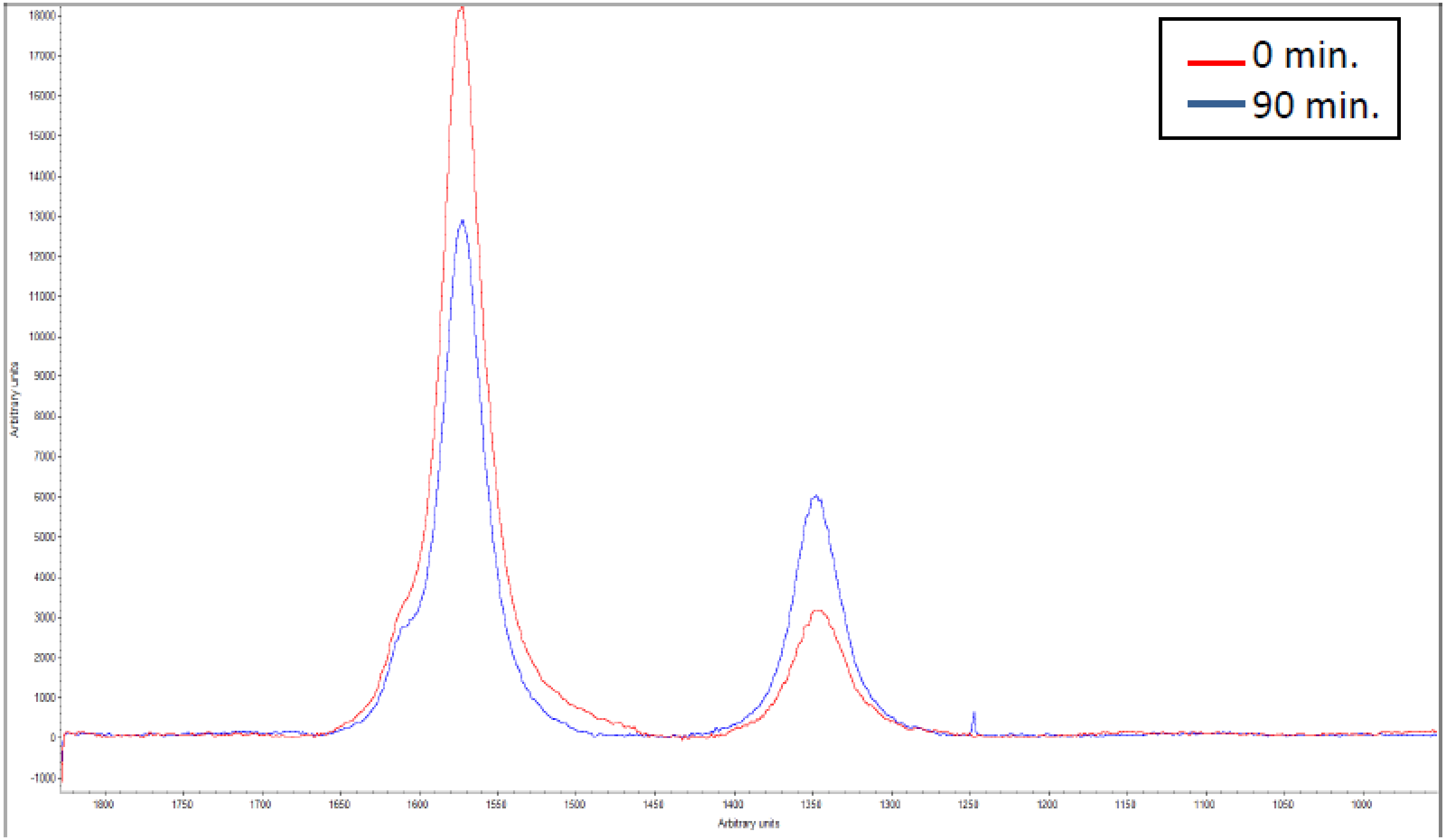
AR 5333	Time (min)		Disorder band					
		G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	18286.1	4830.6	1570.8	0.264	674830.0	137498.6	0.204
	20	14534.4	5479.4	1569.7	0.377	528274.4	171094.2	0.323
	90	13998.4	5140.9	1569.2	0.367	488926.5	145357.8	0.297

EtOH functionalized (#5333)



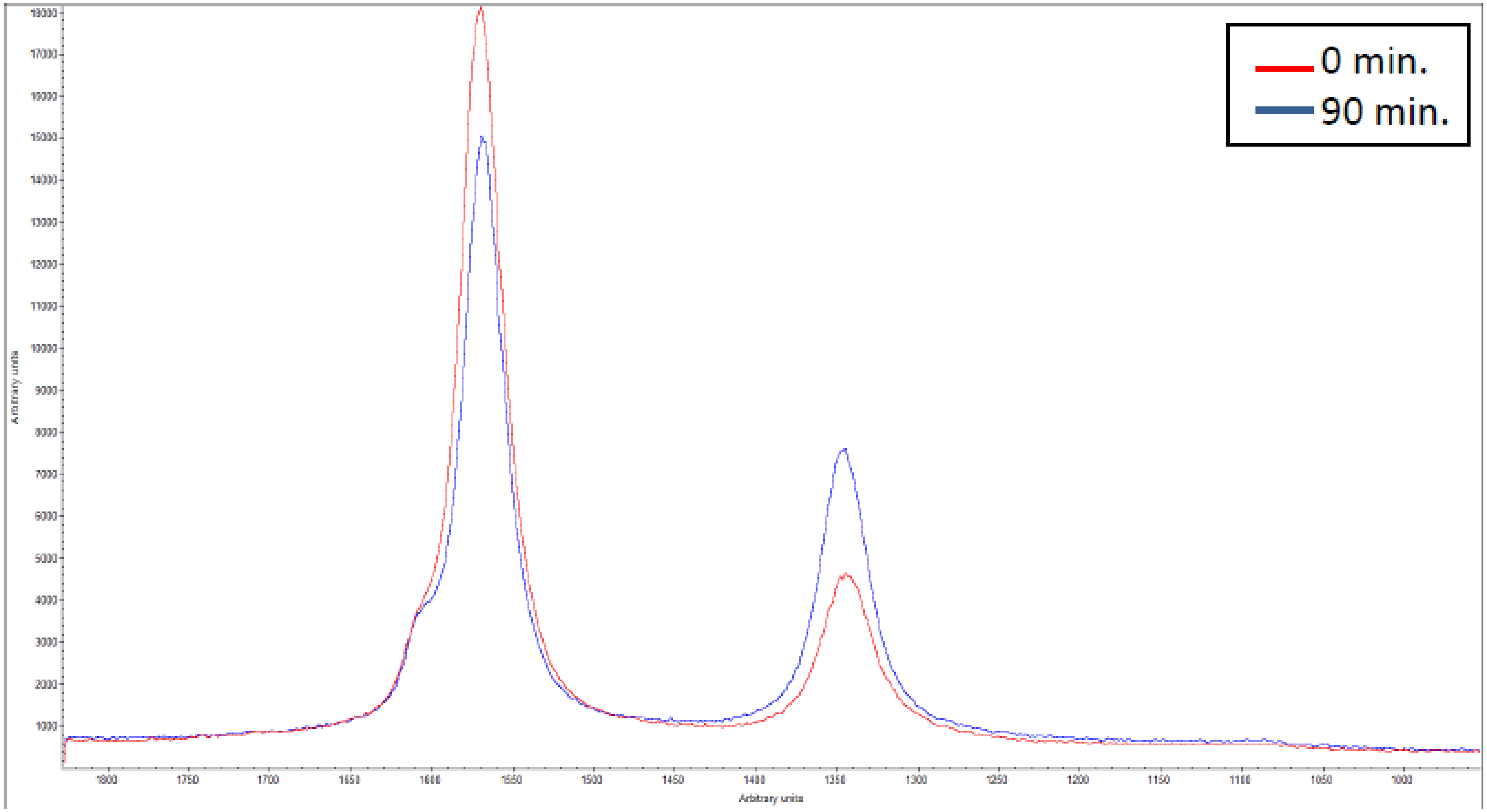
EtOH JSB 11391	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	15330.3	4718.8	1573.8	0.308	598052.7	141972.4	0.237
	90	15606.3	6699.2	1575.8	0.429	557340.1	189818.6	0.341

PrNH2 Functionalized (#5333)



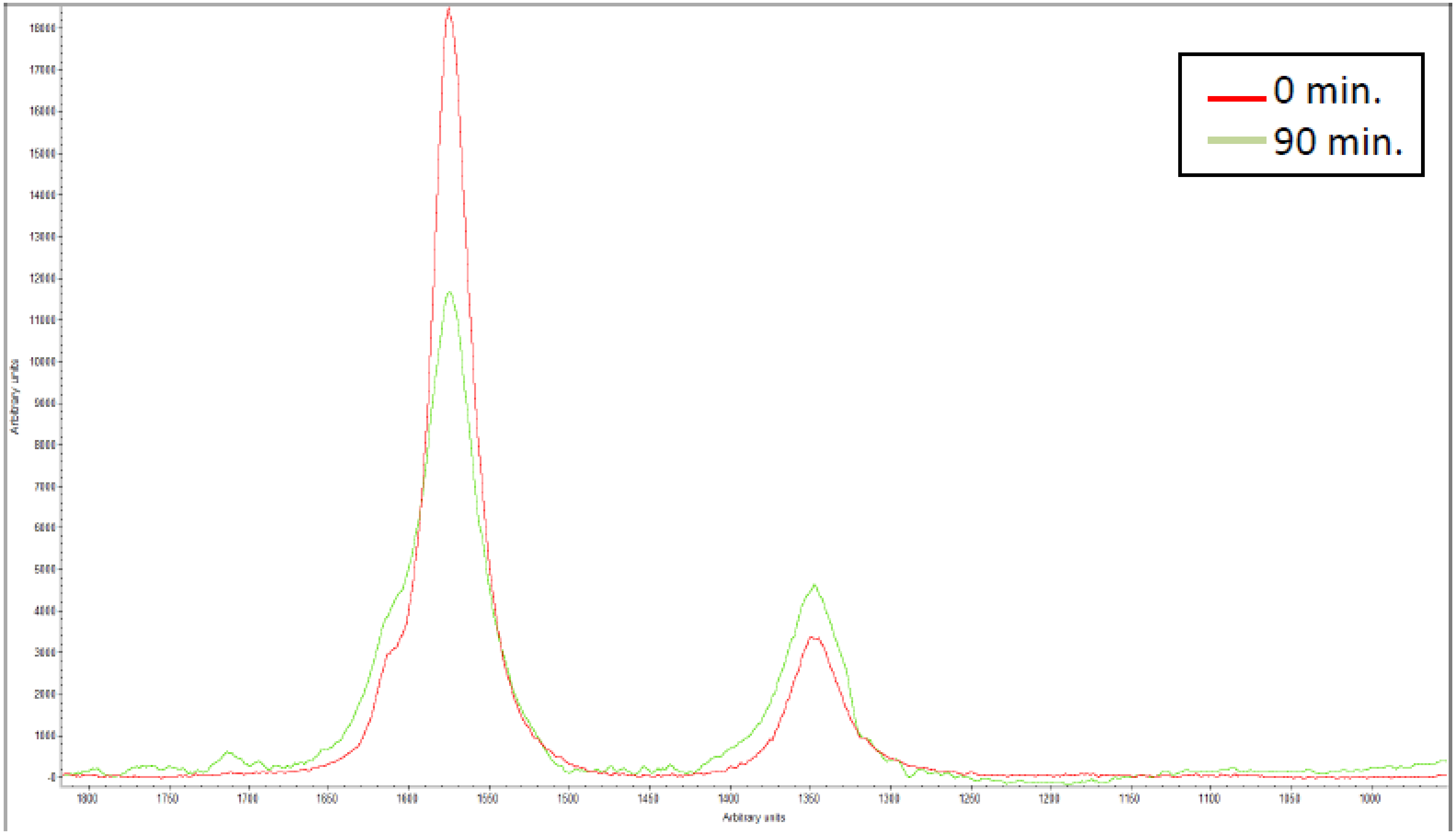
PrNH2 JSB11471	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A (G-band)	A (D-band)	A_D/A_G
	0	20435.0	5324.6	1572.3	0.261	735678.1	117483.5	0.160
	90	14246.4	7280.9	1572.3	0.511	523149.3	222635.6	0.426

Unfunctionalized 15% Prestrain (#5333)



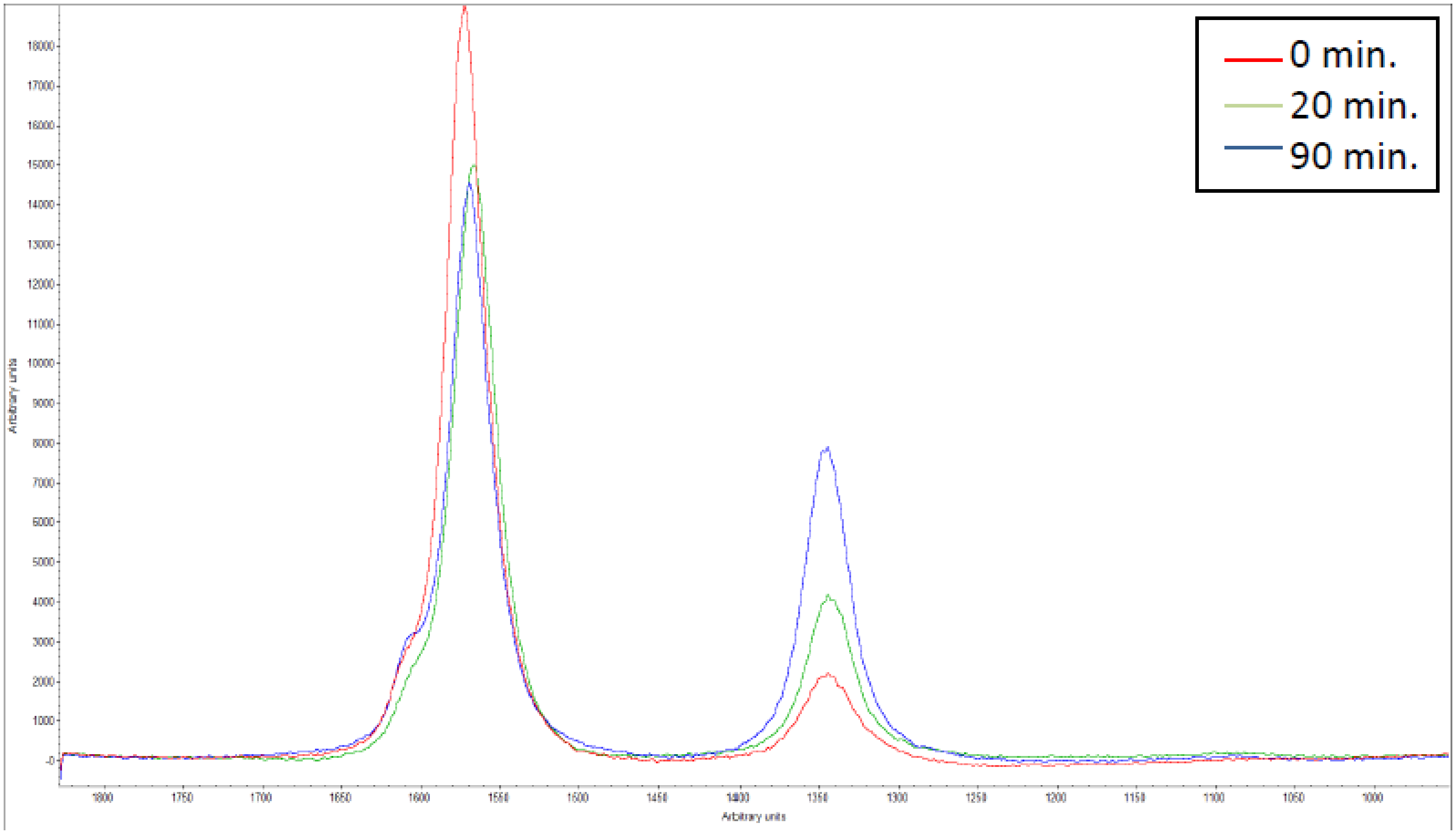
15% Prestrain JSB11652	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	18113.4	4642.4	1569.8	0.256	667741.2	132089.3	0.198
	90	15015.8	7636.5	1569.3	0.509	532588.3	231963.9	0.436

EtOH 13.5% Prestrain (#5333)



EtOH 13.5% Prestrain JSB11611	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	19842.3	4546.0	1575.3	0.230	665729.8	116935.8	0.176
	90	12306.5	3960.5	1576.4	0.322	492436.8	159288.9	0.323

AR 4371 (CNT sheets for panel fab)



AR 4371	Time (min.)	G band (~ 1570 cm-1)	D band (~1350 cm-1)	G-band location	D/G	A(G-band)	A (D-band)	A_D/A_G
	0	19993.2	2979.7	1573.9	0.149	736802.9	84292.9	0.114
	20	16064.6	4804.8	1566.4	0.299	614848.9	147794.5	0.240
	90	18539.3	6846.4	1569.5	0.369	685277.1	196265.6	0.286